Hydrogen from Biomass for Urban Transportation

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Georgia Institute of Technology, Atlanta, GA
Enviro-Tech Enterprises Inc, Matthews, NC

Objectives

- Undertake the engineering research and pilot-scale process development studies to economically produce hydrogen from biomass such as peanut shells.
- Educate and train underrepresented minorities to enhance diversity in the nation's workforce in the energy area.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- F. Feedstock Cost and Availability
- G. Efficiency of Gasification, Pyrolysis and Reforming Technology

Approach

- Develop feedstock supply, process economics and deployment strategies.
- Design, construct, integrate and test pyrolysis-reformer pilot reaction unit.
- Undertake long term (1,000 hours) testing of the performance of the catalyst.
- Design, construct and test the hydrogen separation and storage unit.
- Develop an environmental and technical evaluation method based on analytical monitoring of process streams.
- Develop partnerships, collaborations and education and training programs.

Accomplishments

- Continued developing a model of network process steps to account for feedstock, location, process, and the uncertainties in these factors.
- Collected bio-oil and determined solubility parameters and physical property estimation methods of the components of the bio-oil product of peanut shell pyrolysis.

- Completed system modifications, integration and 100-hour pyrolysis-reformer run for long term catalyst testing.
- Completed analysis of the data for the 100-hour long term catalyst testing.
- Identified potential agricultural uses of the carbon product from the pyrolysis unit.
- Developed plans for 1,000-hour long term testing of the catalyst and process for Phase 3.
- Initiated partnership and collaboration with the University of Georgia, Athens, to move the pyrolysis-reformer pilot unit to their Bioconversion Center facilities in Athens, GA.
- Initiated evaluation of approaches to hydrogen separation and storage, including pressure swing adsorption (PSA) and Quantum's technology for hydrogen storage.
- Held Phase 3 project review meetings at Clark Atlanta University and the University of Georgia, Athens.

Future Directions

- Complete development of models and solutions.
- Perform solubility and physical property measurements and estimations.
- Complete extraction studies and the evaluation of phenolates as co-products for adhesives.
- Modify pyrolyzer, reformer, analysis and other process units for long term testing.
- Design, install and test preheater and PSA units.
- Install new sensors and process control system software in pilot unit.
- Move and integrate units at the University of Georgia Bioconversion Center.
- Perform shakedown run of the integrated system.
- Complete the proposed 1,000 hours of long term operation.
- Complete the engine tests for stationary applications.
- Complete all partnership arrangements.

Introduction

Biomass can be converted to hydrogen by two distinct strategies: 1) gasification followed by shift conversion and 2) pyrolysis of biomass to form a bio-oil that can be subsequently converted to hydrogen via catalytic steam reforming and shift conversion. This project uses the latter approach, which has the potential to be cost competitive with current commercial processes for hydrogen production [1]. The process has been demonstrated at the bench scale at the National Renewable Energy Laboratory (NREL) using model compounds and the carbohydrate-derived fraction of bio-oil [2,3]. The concept has several advantages over the traditional gasification technology. Bio-oil is easily transportable, so the second step (steam reforming) can be carried out at a different location, close to the existing infrastructure for hydrogen use or distribution. The second advantage is the potential for production and recovery of higher-value co-products from bio-oil that could significantly impact the economics of the entire process.

The project focuses on the use of agricultural residues such as peanut shells to produce hydrogen for urban transportation using the pyrolysis-reforming technology. Specifically, a pilot-scale reactor on site at Scientific Carbons Inc.-a small company in Blakely, Georgia, that produces activated carbon by pyrolysis of densified peanut shells-is being used to test the concept. The primary focus of Phases 1 and 2 of the project was to undertake the process development studies in the use of the large quantities of peanut shells produced in Georgia as feedstock for the proposed pyrolysis-steam reforming process. Phase 1 designed, constructed and tested the reformer unit. In Phase 2, Scientific

Carbons's pilot-scale pyrolyzer, which has a feed rate of 50 kg/hour, was integrated with the reformer and used to perform a demonstration of the process to convert the off-gas of the peanut-shell carbonization process to hydrogen. The integrated pilot process was successfully tested for 100 hours. Phase 3 will make further modifications and perform a 1,000-hour long term performance testing of the catalyst and pilot system. The process could be modified and expanded to run a variety of other feedstocks and to make a range of alternative products.

Approach

The approach used to conduct the study is based on six main tasks:

1. Feedstock supply, process economics, and deployment strategies (modeling, extraction and property estimation): Literature data and thermodynamic models were employed to evaluate a large number of organic solvents for the extraction of phenol from aqueous bio-oils. Several good solvents were identified, and extractions were carried out on bio-oil samples provided by NREL. Process models for feedstock supply and deployment strategies were developed.

2. Reactor modifications and shakedown: Modifications in the pyrolyzer and reformer were made, and the entire system, including the pyrolyzer, reformer, and analytical instruments, was integrated and tested. The pyrolyzer unit achieves its heat requirements through the use of a rich burning natural gas burner. A computer is used to track the temperature and pressure drops across the reactors.

3. Long term catalyst testing: The pilot unit was operated in Phase 2 for 100 hours for the long term catalyst testing.

4. Hydrogen separation, storage and utilization: The effort in hydrogen separation is focused on the use of pressure swing adsorption (PSA) for the separation of the hydrogen from carbon dioxide. After the baghouse and condenser, the reformer gas will be dried and compressed before being sent to the PSA system. The current plans are to use an accumulator to store the hydrogen before sending it into an engine for performance testing.

5. Environmental and technical evaluation: A hydrogen analyzer and a gas chromatograph were set up to continuously monitor on line the gas composition and the performance of the reformer bed.

6. Partnership building and outreach: The project team initiated discussions with the University of Georgia (UGA) to move the pilot unit from Blakely, Georgia, to the Bioconversion Center facilities at UGA. The idea was enthusiastically received by UGA. Several meetings were held among the project partners and UGA at Clark Atlanta University and UGA. The current plans are to move the unit to the Bioconversion Center facilities in the summer of 2003.

Results

Figure 1 shows photographs of the pilot unit, its components and the flares from the pyrolyzer and reformer units. The temperature and pressure profiles across the reformer and orifice plate are depicted in Figure 2. The figure indicates that the 100 hours operation was fairly stable without any plugging in the plate or flow lines. No hot spots developed within the fluidized bed reactor.

The composition profile of the effluent gas from the reformer is given in Figures 3 and 4. Figure 3 gives the profile over the entire run period, and

Figure 1. Pictures of the Pilot Plant Unit, Components and Flares

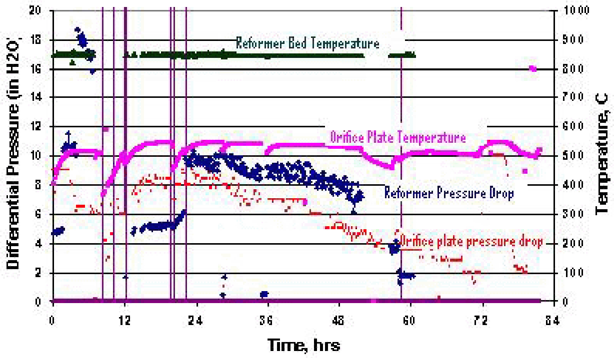

Figure 2. Temperature and Pressure Profiles of Reformer and Orifice Plate

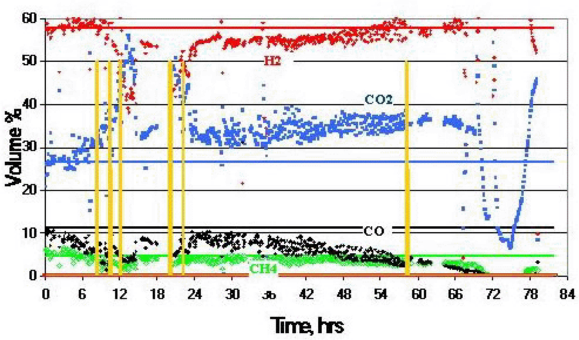

Figure 3. Composition Profile of the Reformer Gas over the Long-Term Run Period

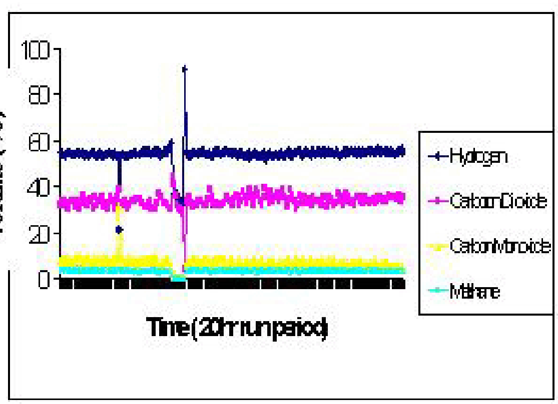

Figure 4. Gas Composition over a 20-hr Period During the Long-Term Catalyst Test

Figure 4 gives the profile of a 20-hour section. The average gas composition (volume % on dry and nitrogen-free basis) over the run period is summarized in Table 1. Also shown in Table 1 are the yields of char, water, bio-oils and gas obtained in the pyrolysis unit. The results show about 60% hydrogen, 25% carbon dioxide, 10% carbon monoxide and 5% methane in the reformer gas. The pyrolysis resulted in about 30% char, 30% water, 30% bio-oils and 5% gases.

Table 1: Yields and Gas Composition for the 100-hour Run

Pyrolyzer (Yields %)		Reformer Gas Product Composition, (% Dry N_2-free basis)	
Char	32	Hydrogen	57
Water	32	Carbon Dioxide	26
Bio-Oils	31	Carbon Monoxide	12
Gases	5	Methane	5

Conclusions

- Demonstrated successfully pyrolysis-reformer concept for 100 hours operation.
- Discovered agricultural uses and carbon sequestration strategy via novel carbon slow release sequestered fertilizer.
- Identified economical co-product options for bio-oils, e.g., adhesives.
- An engine will be run successfully with the product gas with significant reduction of NO_x.
- Further R&D: over 1,000 hours operation and higher hydrogen production rate could lead to economically competitive hydrogen and a viable integrated bioconversion process.

References

1. Mann, M.K. 1995. “Technical and economic analyses of hydrogen production via indirectly heated gasification and pyrolysis,” in Proceedings of the 1995 Hydrogen Program Review, Vol. 1, NREL/CP-430-20036-Vol. 1, pp. 205-236.

2. Wang, D., S. Czernik, D. Montané, M. Mann, and E. Chornet, 1997, I&EC Research, 36, 1507-1518.

3. Wang, D., S. Czernik, and E. Chornet, 1998, "Production of Hydrogen from Biomass by Catalytic Steam Reforming of Fast Pyrolysis Oil", *Energy&Fuels*, 12, 19-24.

FY 2003 Publications

1. Annual Project Review Presentation made at the Hydrogen, Fuel Cells and Infrastructure Review Meeting at Berkeley, CA, May 18-22, 2003

2. Semiannual report on project submitted to the Department of Energy in April 2003

3. Evans, R; E Chornet, S. Czernik, C. Feik, R. French, S. Philips, J. Abedi, Y. Yeboah, D. Day, J. Howard, D. McGee and M. Realff (2002), *Renewable hydrogen production by catalytic steam reforming of peanut shells pyrolysis products,* American Chemical Society (ACS) Paper presented at the Annual ACS Meeting, Boston, MA